Research Article

Hydrochemistry of surface and groundwater along the Coast of Kribi and its environs.

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Abstract

Ground and surface water are the major sources of water supply to the population of Kribi and other communities around this area. A hydrochemical investigation was carried out on the water sources in the area, aimed at identifying the various processes that control the water chemistry, and to assess its quality for domestic purposes. Fifty-six water samples were collected from boreholes, springs, open wells, rivers, rain and tap within the study area during the months of October 2021 and March 2022. Physicochemical characteristics such as pH, electrical conductivity (EC), total dissolved solid (TDS), temperature and major ions were analysed using standard methods. The result indicated that, the pH ranged from 6.3 to 7.0 in the rainy season and 6.2 to 6.5 in the dry season indicating that water in this area is slightly acidic to neutral. EC values ranged from 23.0 to 989μS/cm and 50.9 to 356μS/cm in the rainy and dry seasons respectively and the high EC values in the rainy season indicates high mineralization of the water sources. The TDS ranged from 34.10 to 662.63ppm and 15.41 to 238.52ppm in the rainy and dry seasons respectively. The relative abundance of major ions was $K^+ > Na^+ > Ca^{2+} > Mg^{2+} > NH_4^+$ for cations and $NO_3^- > HCO_3^- > Cl^- > SO_4^{2-}$ for anions. The main water types were: $Ca+Mg-SO_4+Cl$, $Na+K-SO_4+ Cl$, $Na+K-HCO_3$ and $Ca+Mg- HCO_3$ for both seasons. The processes that influence the water chemistry were rock-weathering, mineral dissolution, ion exchange and atmospheric precipitation. The chemical constituents were low and within the international recommended guidelines for drinking water except for high concentrations of NO_3^- (284 mg/l) and K^+ (75.8 mg/l). Water quality index calculated using data for chemical parameters indicated that 96.8% of the water sources was of good to excellent for domestic purposes while 3.2% was of poor water quality. Based on the above parameters, water sources in this area are suitable for domestic purposes.

Key words: Groundwater, surface water, water chemistry, major ions, Kribi.

Résumé

Les eaux souterraines et de surface sont les principales sources d'approvisionnement en eau de la population de Kribi et d'autres communautés autour de cette région. Une étude hydrochimique a été menée sur les sources d'eau de la région, afin d'identifier les différents processus qui contrôlent la chimie de l'eau et d'évaluer sa qualité pour les usages domestiques. Cinquante-six (56) échantillons ont été prélevés dans des forages, des sources, des puits ouverts, des rivières, de l'eau de pluie et de l'eau du robinet dans la zone d'étude entre les mois d'octobre 2021 et mars 2022. Les caractéristiques physicochimiques telles que le pH, la conductivité électrique (CE), les matières solides dissoutes totales (TDS), la température et les ions majeurs ont été analysées. Le pH des échantillons d'eau souterraine variait de 6,33 à 7,0 pendant la saison des pluies et de 6,22 à 6,55 pendant la saison sèche, ce qui indique que l'eau dans cette région est légèrement acide à neutre. Les valeurs de conductivité électrique variaient de 23,0 à 989μS/cm et de 50,9 à 356μS/cm pendant la saison des pluies et la saison sèche respectivement. Les valeurs élevées de la conductivité électrique pendant la saison des pluies indiquent une forte minéralisation des échantillons d'eau pendant cette saison. Les matières solides dissoutes totales (TDS) variaient de 34,10 à 662,63 et de 15,41 à 238,52 pendant la saison des pluies et la saison sèche respectivement. L'abondance relative des principaux ions était la suivante : $K^+ > Na^+ > Ca^{2+} > Mg^{2+} > NH_4^+$ pour les cations et $NO_3^- > HCO_3^- > Cl^- > SO_4^{2-}$ pour les anions. Les principaux types d'eau étaient $Ca+Mg-SO_4+Cl$, $Na+K-SO_4+Cl$, $Na+K-HCO_3$ et $Ca+Mg-HCO_3$ pour les deux saisons. Les processus qui influencent la chimie de l'eau sont l'altération des roches, la dissolution des minéraux, l'échange d'ions et les précipitations atmosphériques. Les constituants chimiques étaient faibles et conformes aux lignes directrices de l'OMS (2017) pour l'eau potable, à l'exception des concentrations élevées de NO_3 (284 mg/l) et de K^+ (75,8 mg/l). L'indice de qualité de l'eau calculé à l'aide des données sur les paramètres chimiques de l'eau indique que 96,8 % des sources d'eau sont bonnes à excellentes pour la consommation, tandis que 3,2 % sont de mauvaise qualité. Sur la base des paramètres ci-dessus, les résultats montrent que les sources d'eau sont adaptées aux usages domestiques.

1.1 INTRODUCTION

The degradation of ground and surface water quality has become a severe universal issue for sustainable development (Adimalla and Jianhua 2019; Li et al. 2019), and it is therefore, very important to understand the hydrogeochemical characteristics of groundwater in particular for sustainable resource development and governance (Huzefa et al. 2020). Groundwater quality depends on natural processes such as rock-water interaction, climatic conditions, geological context, and anthropogenic activities. Natural processes including the mineral precipitation or dissolution, ion exchange, redox condition, residence time, and mixing between different water types may have a great impact on groundwater quality (Wirmvem et al., 2017).

Water quality is a fundamental component of the water supply system (Brodie et al., 2019), which must meet requirements for public, commercial, and industrial activities (Nathanson, 2020). If the concentration of the key physicochemical constituents is not within the required range for a certain water use, then water is deemed unfit for that particular use (Pande and Muharir, 2021). The consumption of water with unfit quality has the potential to result in bad effects. Hence, it is important to understand the quality of the water resource before use (Fahad et al., 2020).

In developing countries, lack of access to clean drinking water adversely affects the population's general health and life expectancy (Adelodun et al., 2021). Clean surface water is radically

subordinate, and people are devoted to groundwater sources (Ighalo et al., 2021). Due to rapid population growth, urbanization, agricultural fertilizers, and planting industrial waste, drinking water quality in many cities and rural areas is affected (Behailu et al., 2017). Severe human health implications, such as cardiovascular and skeletal diseases, infertility, neurotoxicity, etc., are associated with heavy metal exposure. Moreover, exposure to metals results in numerous liver and kidney problems, where some groups of toxicants are considered genotoxic carcinogens (Chabukdhara et al., 2017).

On the African continent, Cameroon is one of the nations endowed with important fresh water resources, including surface waters (streams, rivers, lakes) and groundwater, which often discharge as springs (WHO/UNICEF, 2008). Despite this endowment, supplies of safe drinking water are uncommon in numerous rural and urban areas of the country where the rate of access to drinking water hardly reaches 32% (NSI, 2008).

The town of Kribi, like the majority of the medium-sized cities in Cameroon, encounters enormous difficulties of access to drinking water. In a general way, the only water supplier (CAMWATER) recognized by the State cannot satisfy the needs of the increasing population. Thus, this population tries as it can to be supplied with water of very doubtful potability. Groundwater appears, therefore, to be the most essential source of water for the population in this area and its vulnerability has been recognized as one of the most important problems to be solved. Given the fact that little studies have been conducted in this study area regarding water chemistry and the quality of drinking water. This study therefore aims at identifying the various processes that control the groundwater chemistry and also to assess the water quality for domestic purposes in Kribi and its environs.

1.2. Description of Study Area
1.2.1 Location

The study area is located in the South region of Cameroon, between latitudes 2° and 4° N and longitudes 9° and 11° E (Fig. 1). It covers an area of approximately 1000 km², along the national highway N°7 connecting the cities of Kribi and Edéa.
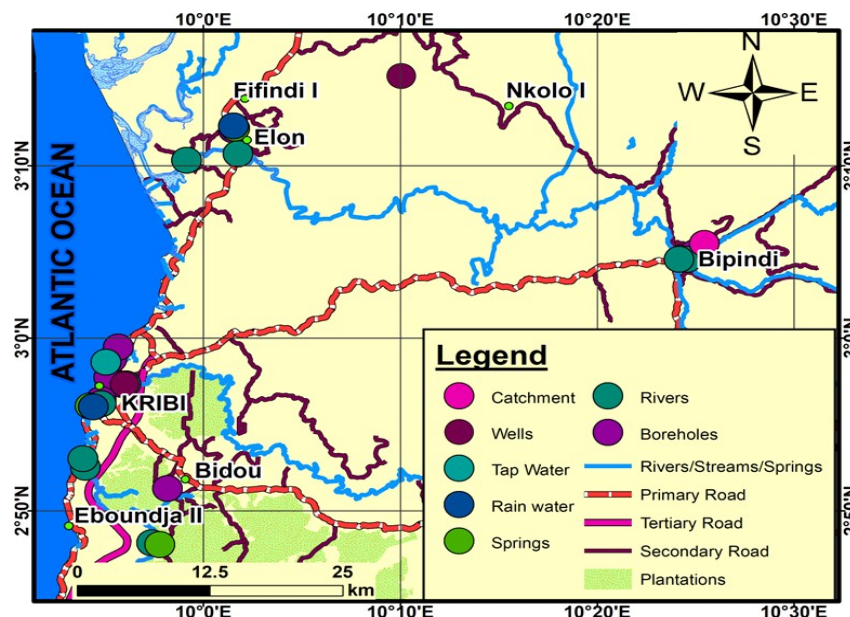

Figure 1: Location map of the study area

267

1.2.2 Climate

The study area local climate is the Equatorial and of Guinean type, which is influenced by the monsoon. The average annual temperature is 26 °C with seasonal differences and an average annual humidity of 60–100%. The climate is bimodal, characterized by two distinct dry seasons (November-March and July-mid-August) and two rainy seasons (April-June and mid-August-October).The average annual rainfall generally decreases with increasing distance from the coast, ranging from 2950/mm/year in Kribi to 2800 mm in Campo. The rainiest months are from August to October (Fig 2).
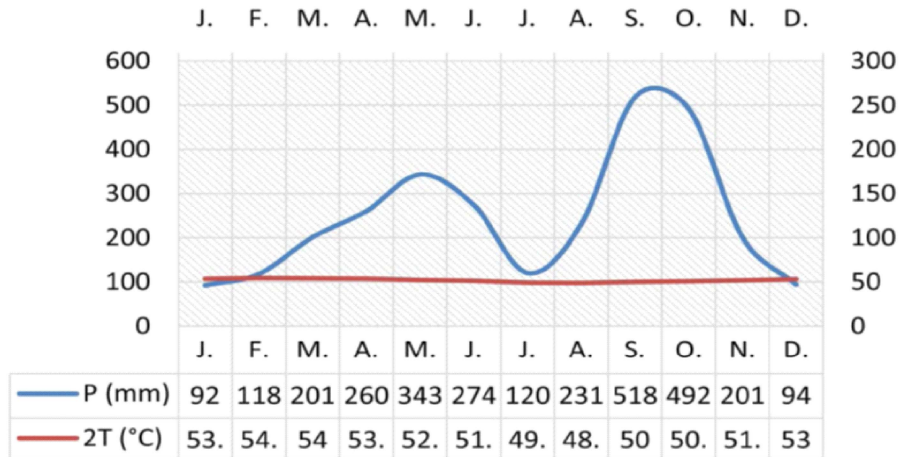

	J.	F.	M.	A.	M.	J.	J.	A.	S.	O.	N.	D.
P (mm)	92	118	201	260	343	274	120	231	518	492	201	94
2T (°C)	53.	54.	54	53.	52.	51.	49.	48.	50	50.	51.	53

Figure 2: Rainfall and temperature diagram of Kribi (Paterne et al., 2021)

1.2.3 Hydrography, hydrogeology and geology.

As far as the hydrography is concerned, Kribi has an extremely dense and dendritic hydrographic network, with a general East-West flow direction imposed by the western slope of the South-Cameroonian Plateau. It has an outlet for important rivers (Nyong, Lokoundjé) and the Lobe water shed (2305Km²).

Hydrogeologically, the aquifers encompass the clay-sandy assembly (CSA) of the Weathering mantle and faults draining (FD) of the basement complex. CSA is a free water aquifer, fed by torrents. Its lateral extension is not significant and is influenced by topography. With regards to the draining faults of the basement complex they are made up of networks of fractures contemporary with the events of the opening and evolution of the Atlantic Basin of Cameroon.

The geological setting of Kribi (Fig 3) belongs to two major lithostructural units of the Lower Nyong and sedimentary formations (Maurizot et al. 1986). The Lower Nyong units are found in the south-west of Cameroon, in the regions of Kribi, Akom II, Lolodorf, Mvengué and Ngomedzap. These units were put in place during the Eburnean orogenesis (2400– 1800 Ma) of ancient Archean rocks of the Ntem basement (Owona et al. 2011). Lithologically, these units are dominated by two large groups of rocks: the foliated series (gneiss, amphibolites, quartzites and other ferriferous formations) that are mainly along the oceanic coast and the intrusive rock complex (syenites, gabbros, dolerites, granites, granodiorites, tonalites and trondhjémites). The sedimentary cover appears in the southern part of Kribi at the Campo zone and in the western part of Edéa at the Douala Basin (Owona et al. 2011). In the Campo region, there is a series of Cretaceous (Aptien) sediments which lie unconformable on the basement rock complex. The main facies of sediments in the area are as follows:

• River and coastal deposits at the mouth of the Nyong and Lokoundjé.

- The sediment pile (conglomerates, sandstones, siltites and shales) of Cretaceous age greater than Lower Pliocene represented by small outcrops on the bank of the Nyong and a 2-km-wide coastal strip in the Campo region. In the western area of Edéa, the sedimentary formations represent a little varied set of conglomerates, marls and limestones of Senonian age, sandstone and Eocene marls and then Pliocene sands. The soils are more or less structural, mainly sandy to sandy-silt. They are poorly permeable on the surface, indicating the presence of an impermeable underlying layer that supports a perched or temporary water table, indicating that despite the reduced flow rate, the soil is able to drain surface water.
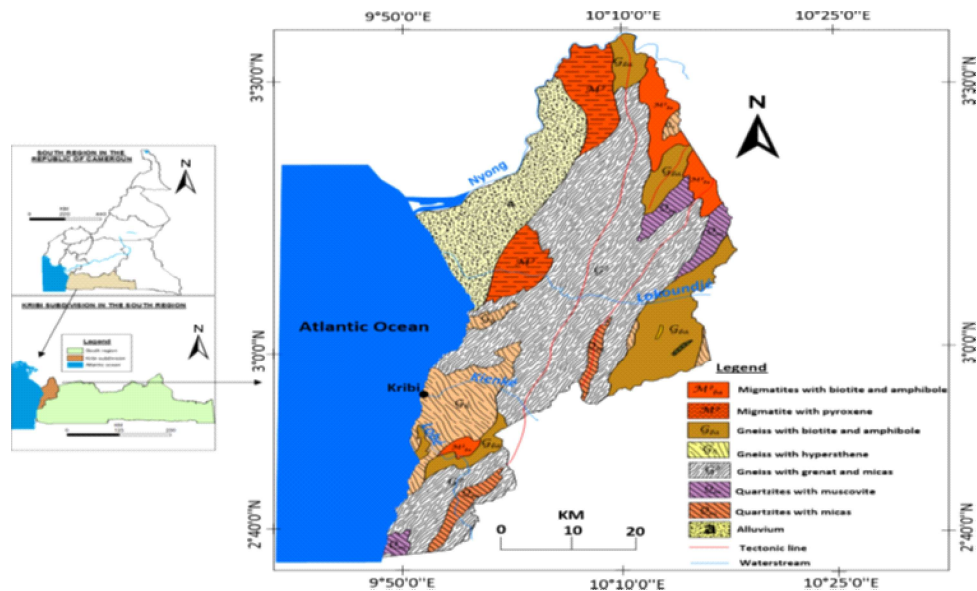

Figure 3: A geological map of the study area (Jose et al., 2021)

Kribi sedimentary sub-basin aquifer system present many challenges in terms of water quality mainly because of limited research that has been carried out on water quality along this area. This lack of sufficient information and knowledge about the water quality in this study area has given birth to significant uncertainties in the projection of the fate of water contamination. It is against this backdrop that this study is assessing the water chemistry and it suitability for drinking in this study area.

2.0 Material and Methods

A total of 56 samples were collected from water sources like rivers, wells, springs, taps, catchments and boreholes for the physico-chemical parameters and a sample location map was obtained using ArcGIS version 10.1 in other to define the sample location points. A total of 31 samples were collected in the rainy season and 25 were collected during the dry season. Sampling was done during the two seasons in order to determine the seasonal variations of the water sources. The rainy season sample collection was done in the month of October, 2021 while the dry season sample collection was done in the month of March, 2022. Sampling was carried out in the morning hours between 6.30 am to 9.00 am and in the evening hours between 4.00 pm to 6.30 pm when the residents were fetching water for the boreholes and wells, while the sampling of rivers and springs was done in the morning hours. On the site sample bottles were rinsed three times using the respective water sample before collecting the samples. The bottles containing the water were then corked, stored in a cool box with ice cubes and transported to the laboratory where they were stored in a refrigerator at a temperature

of below 10^0C (APHA, 2005) to prevent vaporization and biodegradation of analytes while waiting for the physico-chemical analysis (Gichuki & Gichumbi, 2012).

Physical parameters like temperature, pH, electrical conductivity and total dissolved solids were determined on site. The electrode of the pH meter (Model 3150 JENWAY) with a temperature sensor was immersed into the water sample contained in the plastic container and the stable value read. The pH meter was calibrated by immersing the electrode in two buffer solutions of pH 4.01 and 7.00 prepared from capsules of BDH buffer. The pH meter was adjusted to correspond to the standard buffers (4.01 and 7.00). The water sample was placed in a bucket and the electrode was rinsed with distilled water and lowered into the sample. The pH meter was then allowed to stabilize and the pH and temperature of the samples were taken. Electrical Conductivity (EC) and Total Dissolved Solid (TDS) were measured with a digital multi-range conductivity meter manufactured by Hanna Instruments. The instrument was kept clean and standardized with KCl solution before use. The electrode was rinsed with distilled water and lowered into the water sample contained in the plastic container. The conductivity in iScm-1 of the sample was recorded. TDS was also measured by selecting the TDS key while the electrode remained in the water sample used to measure conductivity and the TDS value and mgl-1 was recorded. The collected water samples were then taken to the Laboratory of Environmental Biology and Chemistry at the University of Toyama, Japan for laboratory analyses.

Major ions (Na$^+$, K$^+$, Mg^{2+}, Ca^{2+}, Cl$^{"}$, F$^-$, NO$_3^{"}$, and SO$_4^{2"}$) concentrations were determined using ion chromatography (Metrohm 761 Compact IC). The analytical precision was maintained by running a known standard after every five samples. Samples were filtered through 0.2-ìm filters prior to major ions and dissolved silica (H4SiO4) determination. The H$_4$SiO$_4$ content of the samples was determined by a molybdenum yellow method, using a UV–Vis spectrophotometer (SHIMADZU UVmini-1240). The reproducibility of the analytical procedures was checked by carrying out duplicate analysis. Alkalinity was measured by titration with HCl. The reliability of the data was checked using ionic balance c (IBE) (Appelo and Postma 2005), which shows a charge balance ranging between ±10 %.

Water samples data were standardized and summarised using descriptive statistics: mean, range and standard deviation. Pearson's correlation (r) was used to test the relationship between physical and chemical constituents of the water sources. All the statistics was conducted using a significant level of $\propto$ **=0.5.**

Total hardness was calculated in Excel using the adopted formula 2.5[Ca^{2+}] + 4.1[Mg^{2+}] and WQI was calculated by adopting the Weighted Arithmetical Index method considering thirteen water quality parameters (pH, EC, TDS, Na$^+$, K$^+$, Ca^{++}, Mg^{++}, NO$_3^-$, SO$_4^{2-}$, CL$^-$ total alkalinity, total hardness) in order to assess the suitability of water chemistry for drinking. Various techniques were used to identify the hydrochemical facies so as to understand the hydrogeological processes that influence the water (surface and groundwater) chemistry. These techniques include: Piper diagram (Piper, 1944), Gibbs-Wilcox diagrams (Wilcox 1995) created using Grapher software version 14 Meanwhile Stiff diagram (Stiff, 1951) was obtained with the help of Grapher software version 14 and ArcGIS packages version 10.1. The equilibrium diagrams and saturation index calculations were carried out using the PREAQC software and Excel packages.

3.0 RESULTS
3.1 Suitability of water sources for drinking.

3.1.1 Physico-chemical parameters of water sources.

Temperature collected for all the water samples during the period of sampling ranges from 24.3 - 29.3 ^{0}C in the rainy season and from 27.2 –34.8 ^{0}C in the dry season. Few samples in the dry season did not fall within the WHO guidelines of 30 ^{0}C (WHO, 2017). The pH values for the rainy season samples ranged from 6.33 to 7.0 with a mean of 6.85 and standard deviation of 0.227147. For the dry season, the pH ranged between 6.22 and 6.55 with a mean of 6.37 and standard deviation of 0.105707. The EC values for the rainy season ranged from 50.9 to 989 μS/cm with a mean of 231.82, and standard deviation of ±297.33. During the dry season, the EC ranged between 23 and 356 with a mean of 106 and standard deviation of ±113.07.Meanwhile in the dry season, the TDS values ranged between 15.41-238.52 mg/l with a mean of 71.02 ±75.75446 mg/l and the TDS values for rainy season samples ranged between 34.103- 662.63 mg/l with a mean value of 188.8221 ±199.2141 mg/l
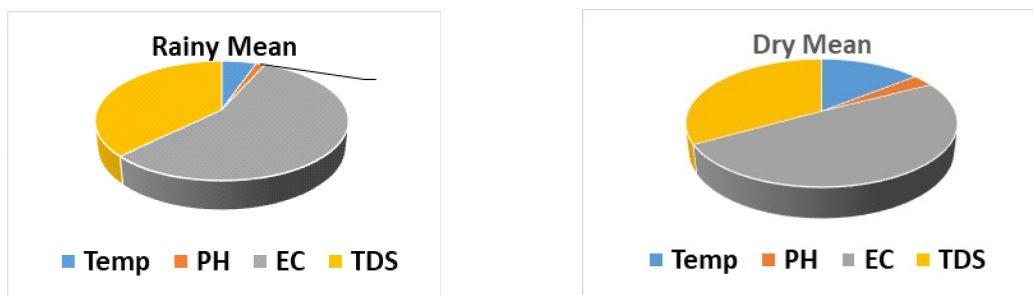

Figure 4: Seasonal variation in the physico-chemical parameters.

3.1.2 Cations Chemistry

Potassium (K^+) was analyzed, and during the rainy season, values ranged from 0.1-75.3 mg/L, with a mean concentration of 12.45±15.32 mg/L. River Morgue downstream (MS29) had the lowest concentration (0.1 mg/L), while Dombe well (MS$_2$) recorded the highest concentration at 75.3 mg/L. In the dry season, the samples recorded the highest concentration at river Morgue upstream (MS$_{25}$) with a value of 75.8 mg/L, and the lowest value was observed at Kieke river downstream, with a mean K^+ concentration of 13.98±14.97 mg/L .Other localities of water sources that recorded high potassium were river Kieke upstream(MS$_1$), Nziou borehole(MS$_5$), Elabe borehole(MS$_6$), Mboa Manga borehole (MS$_{10}$), Mboa Manga (MS$_{11}$), Lobe river upstream(MS$_{15}$), Lobe river downstream (MS$_{16}$), Lokoundje (MS$_{20}$), Bipindi borehole(MS$_{24}$). The maximum permissible limit of K^+ by WHO (2017) is 12 mg/l and this study revealed that 36% and 24% were out of the WHO guidelines for rainy and dry season respectively (Fig 5).
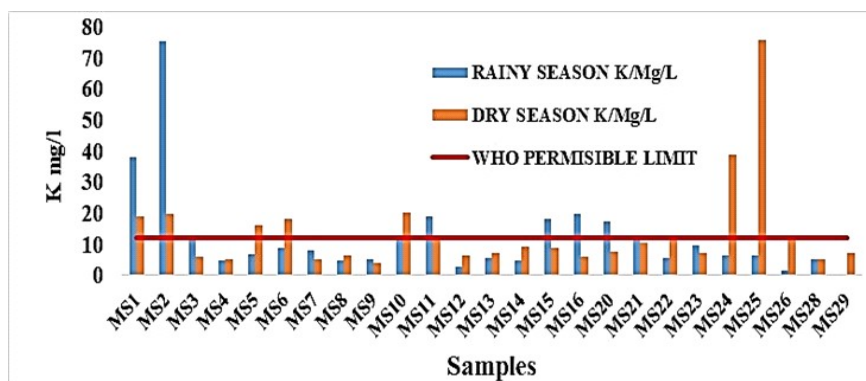

Figure 5: Seasonal Variation in K^+ for both seasons

The concentration of sodium (Na^+) in the samples ranged from 0.2 – 28.7 mg/l (table 1). Both seasons were compared with the WHO guidelines of 50 mg/l, the values were below the recommended guidelines and hence there were within standard. The concentration of Mg^{2+} for the rainy season samples ranged from 0.277 -13.2 mg/l (table 1). All the samples collected and analysed were within the WHO, 2017 guidelines of 50 mg/l. The concentration of calcium for the rainy reason samples ranged between 0.18 – 25.4 mg/l (table 1). All the samples for both seasons were with WHO, 2017 guidelines.
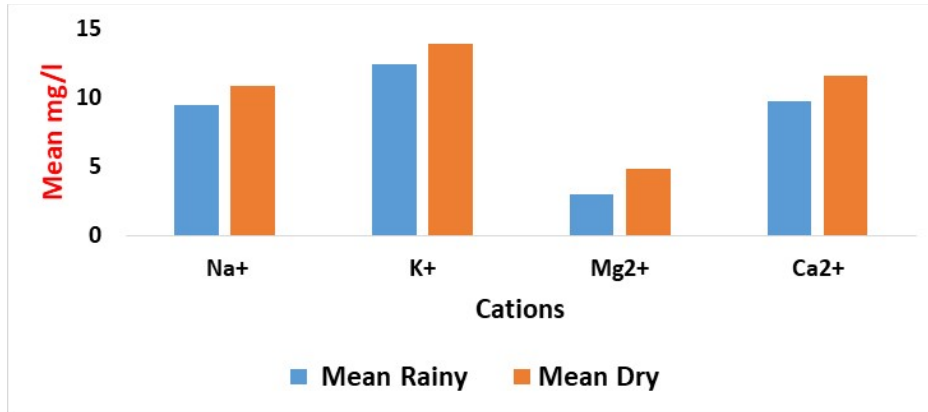

Figure 6: Seasonal variations in cations mean

3.1.3 Anions Chemistry

The chloride concentration for both seasons ranged from 0.03 to 43.89 mg/l (table 1). All the water samples were within the WHO, 20117 guidelines. The fluoride concentration for both seasons samples ranged from 0.01 -3.65 mg/l and 96 % of the water samples were within the WHO, 2017 guidelines of 1.5 mg/l and 4% were out of the guidelines. The concentration of SO_4^{2-} for both seasons ranged from 0.011 mg/l to 8.21 mg/l (table 1). All water sources sampled were within the desired WHO, 2017 guidelines of 200 mg/l. Bicarbonate (HCO_3^-) concentration in water samples in both season ranged from 0.012 mg/l to 56.2 mg/l (table 1). Nitrate (NO_3^-) concentrations in both seasons samples ranged from 0.65 mg/l to 284 mg/l (table1) and 28% and 36% were out of the WHO, 2017 guidelines of 50 mg/l in the rainy and dry season respectively.
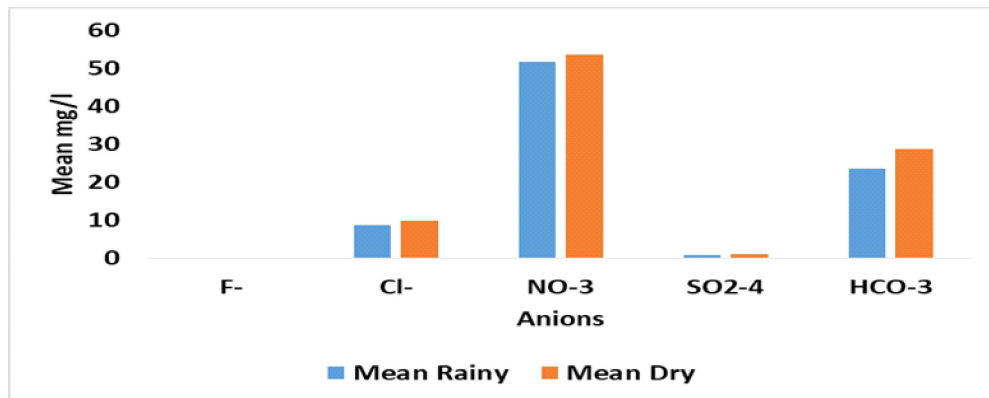

Figure 7: Seasonal variations in anions mean

Table 1: Statistical summary of physico-chemical parameters of water samples in the study area.

Variables	Rainy Season				Dry season				
	Min	Max	Mean	±SD	Min	Max	Mean	±SD	WHO (
Temp(^{0}C)	24.3	29.3	26.58	1.49	27.2	34.8	30.52	1.96	0-30^{0}C
pH	6.33	7	6.85	0.23	6.22	6.55	6.38	0.11	6.5-8.5
EC (µS/cm)	50.9	989	281.82	297.33	23	356	106	113.07	750
Na^+	0.2	27	9.52	7.95	2.1	28.7	10.84	7.69	50
K^+	0.1	75.3	12.45	15.32	4.12	75.8	13.98	14.97	12
Mg^{2+}	0.277	11.6	3.05	2.74	0.61	13.2	4.88	2.80	50
Ca^{2+}	0.18	24.6	9.73	6.67	2.68	25.4	11.61	6.40	75
F^-	0.01	3.65	0.27	0.74	0.02	1.021	0.19	0.26	1.5
Cl^-	0.03	43.2	8.85	10.21	0.21	43.89	9.69	10.37	250
NO_3^-	1.02	266	51.82	71.46	0.65	284	53.57	72.96	50
SO_4^{2-}	0.011	7.01	0.81	1.47	0.06	8.21	1.07	1.75	200
HCO_3^-	0.012	55.2	23.53	18.59	5.9	56.2	28.65	19.06	350
TDS	34.103	662.63	188.82	199.21	15.41	238.52	71.02	75.75	500
TH		109.06	35.79	26.41	9.20	117.62	49.01	26.74	300

Table 2: Pearson's correlation coefficients for physico-chemical parameters of water source.

	Na^+	K^+	Ca^{2+}	Mg^{2+}	Cl^-	F^-	HCO_3^-	SO_4^{2-}	NO_3^-	TDS	EC	PH
Na^+	1											
K^+	.451*	1										
Ca^{2+}	0.375	.549**	1									
Mg^{2+}	0.297	.736**	.780**	1								
Cl^-	.603**	.869**	.678**	.784**	1							
F^-	-0.095	0.166	-0.116	0.043	0.124	1						
HCO_3^-	0.371	-0.169	-0.2	-0.147	-0.066	-0.293	1					
SO_4^{2-}	0.207	0.35	0.345	0.219	0.386	-0.04	0.079	1				
NO_3^-	0.32	.912**	.697**	.891**	.865**	.875**	-0.391	0.201	1			
TDS	.585**	-0.195	-0.319	-0.247	-0.109	-0.2	.616**	-0.238	-0.334	1		
EC	.585**	-0.195	-0.319	-0.247	-0.109	-0.2	.616**	-0.238	-0.334	1.000**	1	
PH	.450*	0.221	0.059	0.174	0.261	-0.34	.474*	0.073	0.077	0.395	0.395	1
TEMP	0.274	-0.089	-0.161	-0.146	-0.147	-0.364	0.263	-0.145	-0.274	.600**	.600**	0.202

* Correlation is significant at the 0.05 level (2-tailed).
** Correlation is significant at the 0.01 level (2-tailed).

3.1.4 Total Hardness (TH)

The total hardness of water samples in the rainy season ranged from between $0 – 109.06$ $CaCO_3$ (mg/l) and from $9.201 – 117.62$ $CaCO_3$ mg/l in the dry season (table 3). According to this study, water samples ranged from soft to moderately hard in the rainy season and slightly hard to moderately hard in the dry season. In the rainy season 9.7% is classified as soft and 74.2%, 16.1% are classified as slightly hard and moderately hard respectively. Meanwhile 68% and 32% are classified as slightly hard and moderately hard respectively in the dry season.

Table 3: Groundwater classification based on total hardness (TH) after Driscoll (2009)

Total hardness $CaCO_3$ (mg/l)	Water type	Rainy season		Dry season	
		No of samples	%	No of samples	No of sa
<9	Soft	3	9.7	0	0
9-60	Slightly hard	23	74.2	17	68
60-120	Moderately hard	5	16.1	8	32
120-180	Hard	0	0	0	0
>180	Very hard	0	0	0	0

3.1.5 Water Quality Index (WQI)

The values of the WQI obtained in this study showed that 96.8% of the water is of good to excellent during the rainy season and all of groundwater within the study area have an excellent water quality in the dry season, respectively (table 4), this imply that based on the physicochemical parameter, the water is suitable for drinking purposes. However, 3.2% of groundwater in the area is of poor water quality towards Dombe quarter.

Table 4: WQI classification

WQI	WQI Classification	Rainy season		Dry season	
		No of samples	%	No of samples	No of sa
0 – 25	Excellent	28	90.3	25	100
26 – 50	Good	2	6.5	0	0
51 – 75	Poor	0	0	0	0
76 – 100	Very poor	1	3.2	0	0

3.2 Mechanism controlling Solute Chemistry.

Piper diagram

The piper diagram is a very useful hydrogeochemical tool and it was used in this study to compare the various water samples, determine water type and equally to know the various hydrogeochemical facies. Findings of this study revealed that, the main dominant cation and anion in both season is the alkalis metals (Na +K) and a weak acid (HCO_3^-). Based on their ionic concentrations and relative proportions, four hydrogeochemical facies were identified: $Ca+Mg- SO_4^2 +Cl^-$ (field I), $Na+K- SO_4^2 +Cl^-$ (field II), $Na+K-HCO_3^-$ (field III) and $Ca+Mg- HCO_3^-$ (field IV) in both seasons with field IV dominated hence making $Ca+Mg- HCO_3^-$ the dominant water type in both season (figure 8).
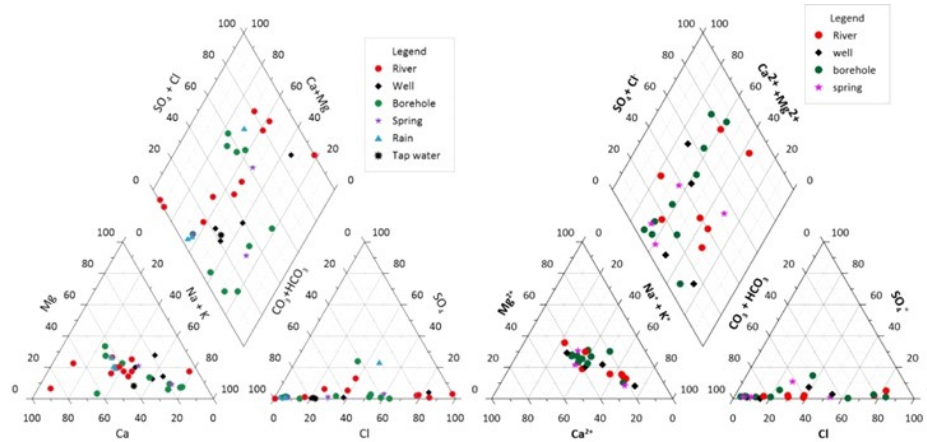
Figure 8: Piper's diagram (Piper, 1944) showing four hydrogeochemical facies that were identified.

Stiff diagram

The sizes and shapes of the stiff diagram were used to determine the water facies and degree of mineralization of the various water sources in both season. The variations in the shapes and sizes depend on water interaction processes and/ or pollution factors that differently affect the study area. The shape of the Stiff diagram in the rainy season (figure 9) suggests that rivers and wells samples were rich in the cations Na^+ and K^+ and in the anion Cl^-, boreholes, springs, catchment and tap samples rich in the cations Na^+ and K^+ and HCO_3^-, meanwhile rainwater samples were rich in Ca^{2+} and HCO_3^-.
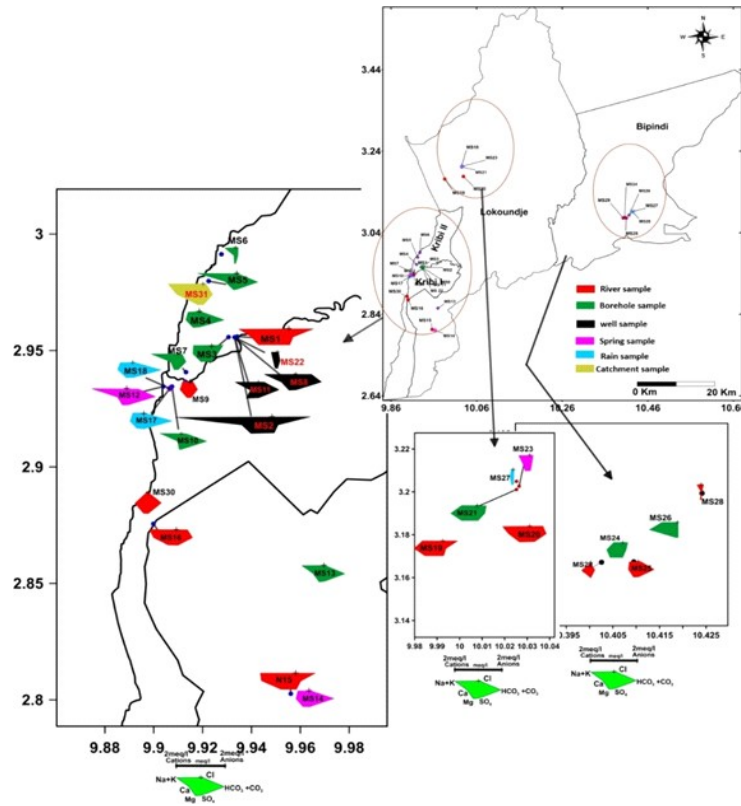

Figure 9: variation in shapes and sizes of the Stiff Diagrams in the raining season.

During the dry season (figure 10), the Stiff diagram suggested that boreholes, wells and springs samples were rich in the cations Na^+ and K^+ and HCO_3^- anion. Rivers samples were rich Na^+ and K^+ and in the anion Cl^- and catchment and tap samples rich in Ca^{2+} and Cl^-.
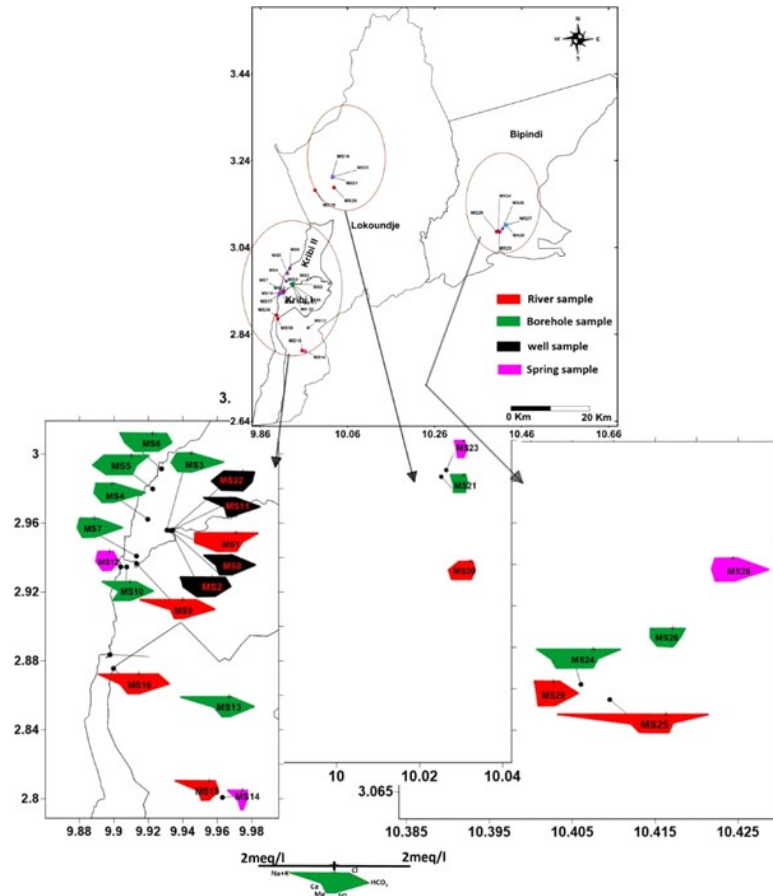
276

Figure 10: variation in shapes and sizes of the Stiff Diagrams in the dry season.
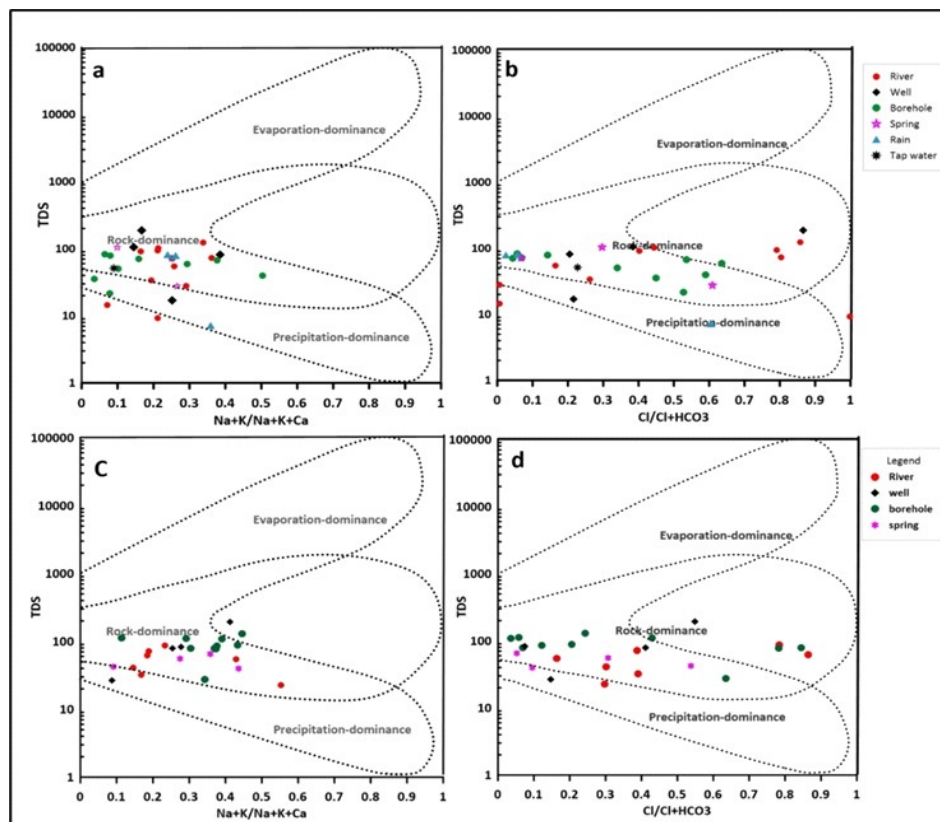

Figure 11: Gibbs (1970) diagram in the rainy and dry season.

From the Gibbs diagrams plots (figure 11), two significant hydrochemical facies were identified, that is Rock- weathering dominance and precipitation. In the rainy season, 26 (83.9%) samples were plotted in the rock-weathering dominance field while for dry season, 22(88%) samples were plotted in the rock-weathering dominance field. During the rainy season 5(16.1%) samples were plotted in the precipitation dominance field while for dry season, 3(12%) samples were plotted in the precipitation dominance field.

Stability diagram

Mineral stability diagram have been used extensively to high-light the most stable silicate mineral phases in the hydrochemistry of surface and groundwater basin. The software PHREEQC was used to calculate the activities of ions such as K^+, Na^+, Ca^{2+} and H_4SiO_4 in both rainy and dry seasons. The stability diagram of K^+-aluminosilicates **(figure 12 c & f)** showed that most of the groundwater samples felt in the stability region of Kaolinite and illite and only one sample felt in the mica stability region. This region shows that kaolinite and illite were in equilibrium.

$2K\,Al\,Si_3\,O_8 + 2H^+ + 2H_2O = Al_2\,Si_2\,O_5\,(OH)_4 + 4Si\,O_2 + 2K^+$……………..(1).
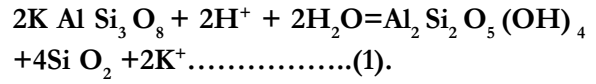
The stability diagram of Na^+, Ca^{2+}-aluminosilicates (H^+-SiO_2) plotted in both rainy and dry seasons indicated that, all the groundwater samples felt on the stability region of kaolinite suggesting that kaolinite is stable or in equilibrium in this area (**figure 12 a , b, d & e).**
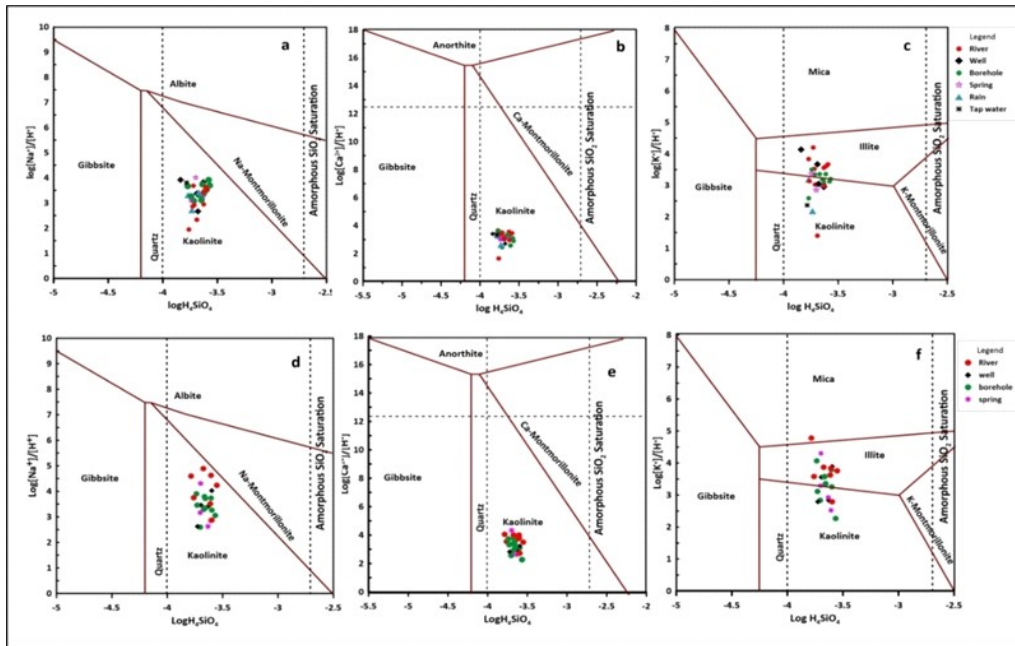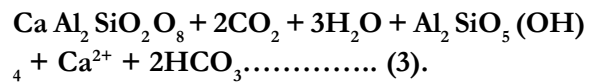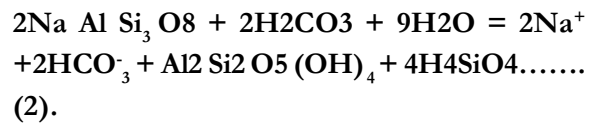
$2Na\,Al\,Si_3\,O8 + 2H2CO3 + 9H2O = 2Na^+ + 2HCO_3^- + Al2\,Si2\,O5\,(OH)_4 + 4H4SiO4$……. (2).

$Ca\,Al_2\,SiO_2\,O_8 + 2CO_2 + 3H_2O + Al_2\,SiO_5\,(OH)_4 + Ca^{2+} + 2HCO_3$………….. (3).

Figure 12. Stability diagram in the rainy and dry season.

Saturation Index

According to Parkhurst et al. (2018) PHREEQC software can be used to calculate the SI values of the minerals in groundwater and this software was used in this study to calculate the SI values. The SI results of this study suggest the trend of water and mineral chemical equilibrium and water–rock interaction in the area. If under saturated (SI < 0), the mineral will be continuously weathered by the groundwater; if oversaturated (SI > 0), the mineral will precipitate; and if SI is equal to 0, the mineral phase will remain in an

278

equilibrium state. According to the hydrochemistry data, the saturation indices of particular minerals were calculated (Table 5& 6). The Saturation Index values of Anhydrite, Aragonite, chalcedony, calcite, dolomite, gypsum etc. are under saturated (less than 0) suggesting that carbonate minerals are continuously weathered by groundwater. This is contrary to the SI values of Goethite, Hematite and Quartz which are oversaturated (greater than 0) suggesting these minerals are precipitated in groundwater.

Table 5: Statistical summary of saturation indices in the rainy season

Mineral	Min	Max	Mean
Anhydrite	-7.03	-3.57	-5.19
Aragonite	-5.08	-0.91	-2.40
Calcite	-4.93	-0.08	-2.20
Chalcedony	-0.51	-0.02	-0.14
Dolomite	-9.17	-3.28	-4.77
Fluorite	-5.77	-1.53	-4.26
Goethite	**5.77**	**8.27**	**6.81**
Gypsum	-6.32	-3.27	-4.86
Halite	-12.33	-7.75	-9.27
Hematite	**-8.90**	**18.54**	**14.50**
Quartz	**-2.55**	**0.41**	**0.21**
SiO2	-6.63	-0.86	-1.37
Talc	-9.11	-4.35	-6.68

Table 6: Statistical summary of saturation indices in the dry season.

Mineral	Min	Max	Mean
Anhydrite	-3.91	-3.06	-3.38
Aragonite	-3.26	-0.90	-1.97
Calcite	-3.12	-0.76	-1.87
Chalcedony	-2.20	-0.06	-0.25
Dolomite	-6.35	-1.51	-3.73
Fluorite	-5.24	-1.50	-3.56
Goethite	**4.81**	**8.90**	**7.03**
Gypsum	-3.66	-2.82	-3.14
Hematite	**11.66**	**19.85**	**16.13**
Quartz	**-0.74**	**0.35**	**0.20**
SiO2	-2.69	-0.88	-1.06
Talc	-10.89	-0.44	-5.21

4.0 DISCUSSION

4.1 Suitability of water sources for drinking based on the physico-chemical parameters

4.1.1 Physico-chemical parameters of water sources.

Temperature is an important physical constituent of groundwater since a variation of this parameter by 10^0C in aquifer may lead to doubling of chemical reactions. In this, temperature has a strong positive correlation **(r=0.6)** with EC (table 2) since in most aquifers temperature is closely associated with it. The results of temperature of this study is similar to the study carried out by Wali SU et al., (2018) in Northern Kebbi State, Nigeria and those gotten by Fantong et al, (2020) in a study that was carried out in Benue River basin- Cameroon. The pH values ranged from slightly acidic to neutral for both seasons. This is contrary to the results obtained by Fantong et al, (2020) and the values ranged from acidic (5.7) to basic (8.9). It is important to know that pH is very essential in water chemistry since it controls the characteristics of several water chemical elements Wali SU et al., (2018). In this study pH showed no very positive correlation with no chemical parameter tested (table 2).The EC in the rainy season was generally very high compared to the dry season. This high EC in the rainy season could be an indication that the water sources around this area are experiencing slight mineralisation due to runoff, infiltration and percolation from dumpsites, agricultural activities and leachate that are located around the water sources. The dry season values of EC that range from 23.0 - 356 μS/cm were within the WHO guidelines of 750 μS/cm and this is similar to the result obtained Garoma et al., (2018) that recorded values between 80–248.96 ìS/cm in the town of Shambu in Ethiopia.

.EC values in groundwater is most at times associated with TDS reason for the perfect positive correlation (r=1) between TDS &EC in this study (table 2).

279

4.1.2 Cations Chemistry

The geology of kribi is composed of Gneisses which are high-grade metamorphic rocks that have been subjected to intense heat and pressure. They are typically banded or foliated and may contain minerals such as quartz, feldspar. Mica and amphibole. This is possible that the high level of potassium in this area could be as a result of natural sources such weathering of mineral containing potassium, such as Feldspars and micas (Appelo and postma 2005) and dissolution of potassium salts like halite from geological formations (Edmunds and Smedley, 2007). Equally it could be coming from anthropogenic sources such as agricultural activities like applying of fertilisers containing potassium and animal manure (USEPA, 2020).To render these water sources potable for drinking we can use the reverse osmosis system or distillation to remove potassium from the water sources (USEPA, 2018). Even though sodium is an essential element in nutrition but the concentration in drinking water still need to be monitor since the joint effect of Na^+ & SO_4^{2-} is associated with hypertension. Calcium in groundwater is beneficial but elevated level often cause water hardness. The trend of concentrations of cations (fig 6) for both rainy and dry season was $K^+ > Na^+ > Ca^{2+} > Mg^{2+}$. This results are contrary to the results obtained by Akoachere et al. (2019) in coastal town of Douala where the results of this study showed that the trend of cations was $Ca^{2+} > Mg^{2+} > K^+ > 4 NH^+ > Na^+$ and $Ca^{2+} > Mg^{2+} > K^+ > Na^+ > 4 NH^+$ in both wet and dry season respectively.

4.1.3 Anions Chemistry

This high level of NO_3 in this study area could be attributed to anthropogenic activities since NO_3^- is driven mainly from oxidation of Ammonia and agricultural fertilisers. High nitrates in drinking water is dangerous as it causes infants-blue baby syndrome. The trend of anions concentration (fig 7) in water samples is $NO_3^{"} > HCO_3^{"} > Cl^{"} > SO_4^{2"}$ in both seasons. These results are contrary to the results obtained by Akoachere et al. (2019) in coastal town of Douala where the results of this study showed that the trend of anions was $HCO_3^{"} > Cl^{"} > SO_4^{2-} > NO_3^- > HPO^-$ and $HCO_3^- > Cl^- > SO_4^{2-} > HPO^{"} > NO_3^-$ in the wet and dry season respectively. Although these studies were all carried out in a coastal areas (Douala and Kribi), their results were contradicting with respect to the abundance of their major ions. Also the study which carried out by Akoachere et al (2019) in the coastal town of Douala showed that all the major ions in both season felt below WHO acceptable limits meanwhile in this study some of the ions like K^+ and $NO_3^{"}$ were above the WHO permissible limits. The hardness is an important criterion for determining the usability of water for domestic and industrial supplies (Nagarajan *et al.* 2009). Hardness can be classified as temporary due to carbonate and bicarbonates or permanent due to sulphate and chlorides of calcium and magnesium. Similar findings were gotten by Akoachere et al, (2019). Hardness of water supply intended for human consumption is between 80 and 100 mg/l Discoll, (2009). However, from the calculated hardness, not all of the water sources were within the permissible limit of the WHO guideline of 100 mg/l.

Al-Omran et al. (2015) found a slight similar range of suitable water from five zones of Riyadh governorate (Nassim, Riyadh main zone, Badiah zones, Ulia and Shifa) but this findings are contrary to the one obtained by Anwar et al., (2014) in Saudi Arabia where by the computed WQI values for the 28 untreated well waters in Hafar Albatin ranged from 102.6 to 597.5, with 14 % of the waters being class (III) "poor water", 39 % were class (IV) "very poor water", and 47 % were class (V) or "water unsuitable for drinking" and when further to give the reasons for the high WQI values

obtained for this study area which were the high values of pH, TDS, Mg^{2+}, $HCO3^{"}$, $Cl^{"}$, $NO3^{"}$, B, and total hardness. Comparing this with our results, the correlation WQI with the physical parameters showed a negative to weak correlation. This could be the possible reasons for the low values of WQI and hence high percentage of excellent water quality.

4 .2 Mechanism controlling Solute Chemistry.

The dissolution of carbonates (Calcite & dolomite) and gypsum are the various sources of Ca^{2+}, Mg^{2+} and HCO_3^- in groundwater. So these elements from piper diagram might have come from the dissolution of carbonate through the action of percolating waters with enhanced CO2 after interaction with the atmosphere. CO2 is unconstrained in to solution by suspension of carbonate, forming Ca-HCO3 or from the dissolution of gypsum. Same findings were gotten by Wali et al., (2018) and Akoachere *et al.*, (2019).Across both season, the degree of mineralisation of the Stiff diagram for both rivers and wells are very high this could be as a result of saline water intrusion along well and river channel due to their shallow nature. The Gibbs diagram is an indication that the dominant mechanism contributing solute to groundwater in the study area is water-rock interaction.Equally the stability diagram is a clear indication that this area has a good drainage condition since previous studies has shown that water samples keeping in equilibrium with kaolinite reflect good drainage conditions. Similar findings were gotten by Biao et al, (2020).

According to Biao et al. (2020), groundwater hydrochemistry is governed by many processes, such as groundwater flows, recharge and discharge processes, and water–rock reactions. Along the groundwater flow direction, hydrochemistry is always affected by minerals weathering in long residence time Wen et al. (2008).

CONCLUSION

The slightly acidic groundwater sources might lead to the dissolution of heavy metals in rocks in the study area. The majority of the groundwater sources were slightly hard to moderately hard waters and the Water quality index calculated using the chemical parameters of water data indicated that 96.8% is good to excellent while 3.2% is of poor water quality, respectively for domestic purposes indicating that most water sources around this area are of good quality with respect to their water quality index of chemical parameters.

The relative abundance of major ions was $K^+ > Na^+ > Ca^{2+} > Mg^{2+} > NH_4^+$ for cations and $NO_3^{"} > HCO_3^{"} > Cl^{"} > SO_4^{2"}$ for anions, respectively. The major ions were within the WHO (2017) guideline values for drinking water except for high concentrations of NO_3^- and K^+ ions of the study area which increases the risk of the population to diseases such as methemoglobinemia, gastric ulcer, cancer and urinary tract diseases. Potassium (K^+) was the dominant cation, while NO_3^- was the dominant anion for all the water sources. The high level of NO_3^- and K^+ ions might be a clear indication of anthropogenic pollution from farmlands and plantation around these sources of water.

The water types in the area were: $Ca+Mg-SO_4+Cl$, $Na+K-SO_4+ Cl$, $Na+K-HCO_3$ and $Ca+Mg-HCO_3$.The degree of mineralisation for both rivers and wells were very high and this could be as a result of saline water intrusion along well and river channel due to their shallow nature.
The main hydrogeochemical processes that influenced the chemical composition of the water sources were simple dissolution, rock weathering, atmospheric precipitation and ion exchange.

Mineral saturation indices suggest that the dissolution of carbonates, sulphates, halites and fluorides were insignificant in the water sources.

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